Simulation of Molecular ALC Spectra using Density Functional Theory

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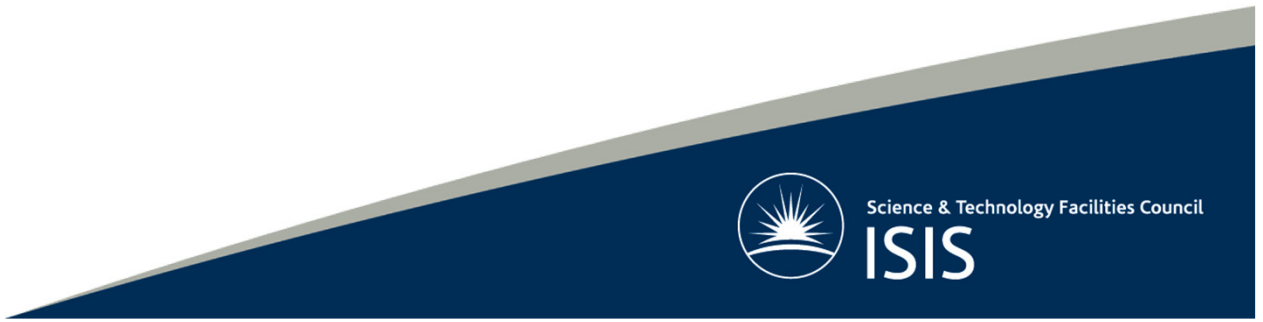
ISIS

ISIS Muon User Meeting 17/09/12



Requirements

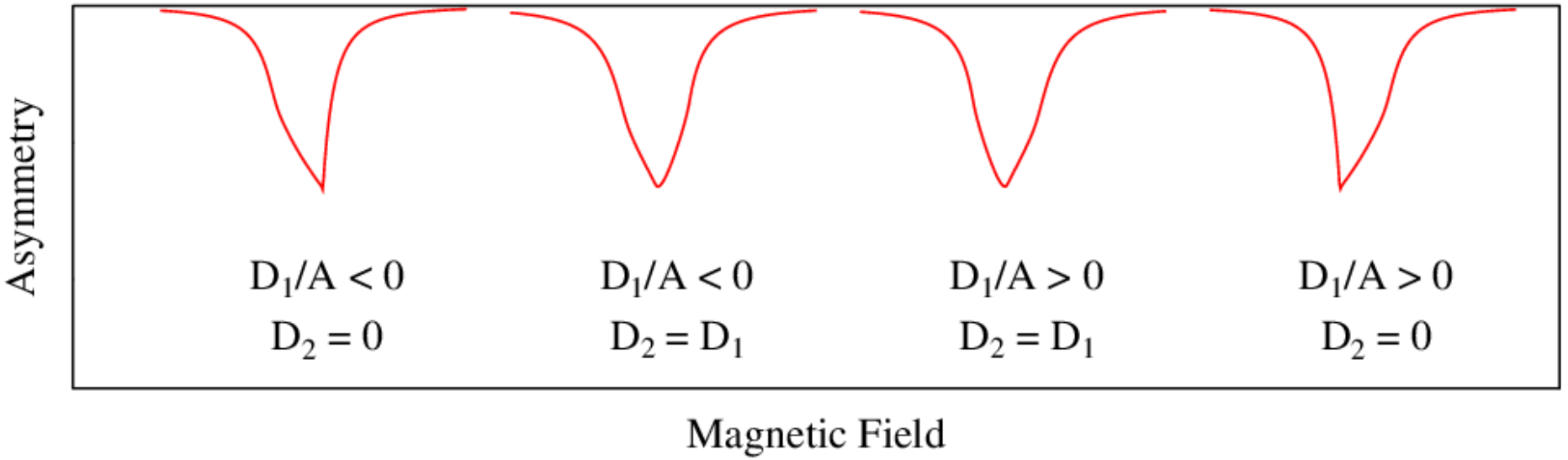
- Efficient calculation of molecular ALC spectra (establish level required for reliable results on the timescale of an ALC experiment)
- Start with low T solid state resonances (needing full hyperfine tensor)
- Aim to include zero point motion as well as thermally excited vibrations
- Validate method against well studied reference systems, e.g. TCNQ, Alq_3, polymers, benzene

Solid State ALC Resonances

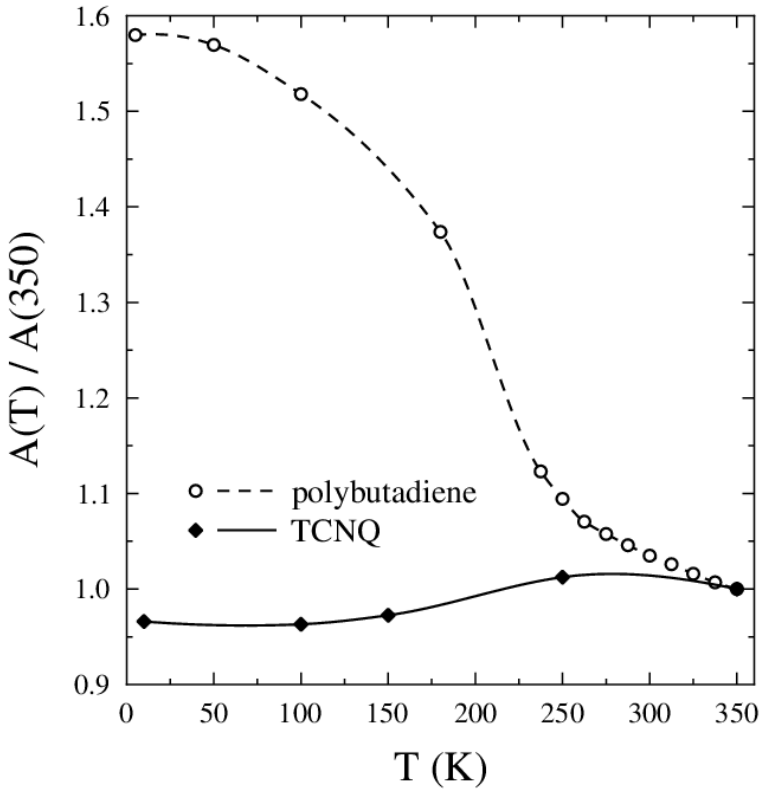
Dominated by Δ_1 resonances where the levels differ only in muon spin

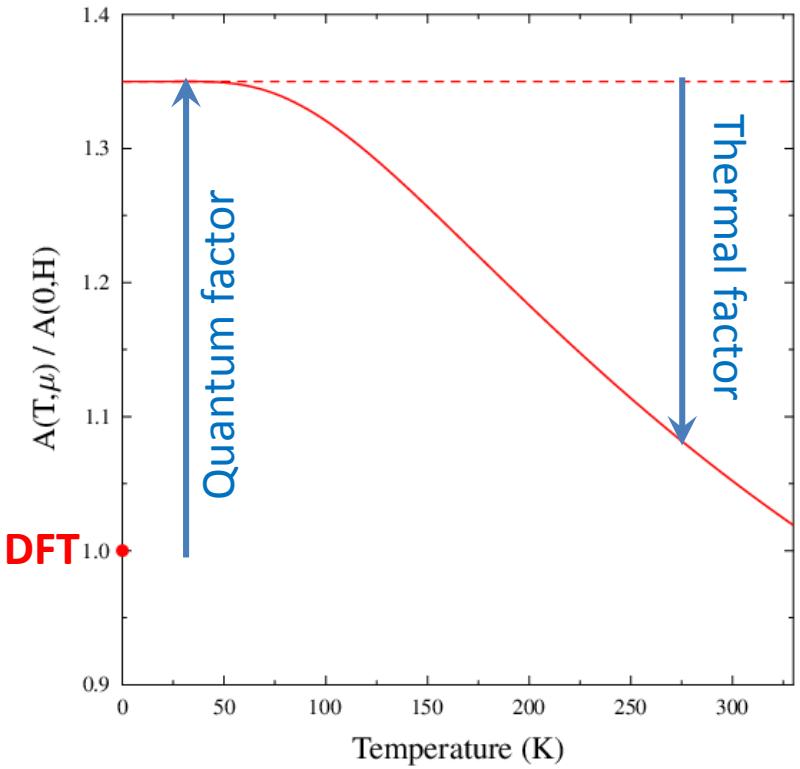
Resonance position determined by the isotropic HFC parameter A

In the static low T limit the line shape is determined by the dipolar parameters D_1 and D_2



Quantum and Thermal Effects

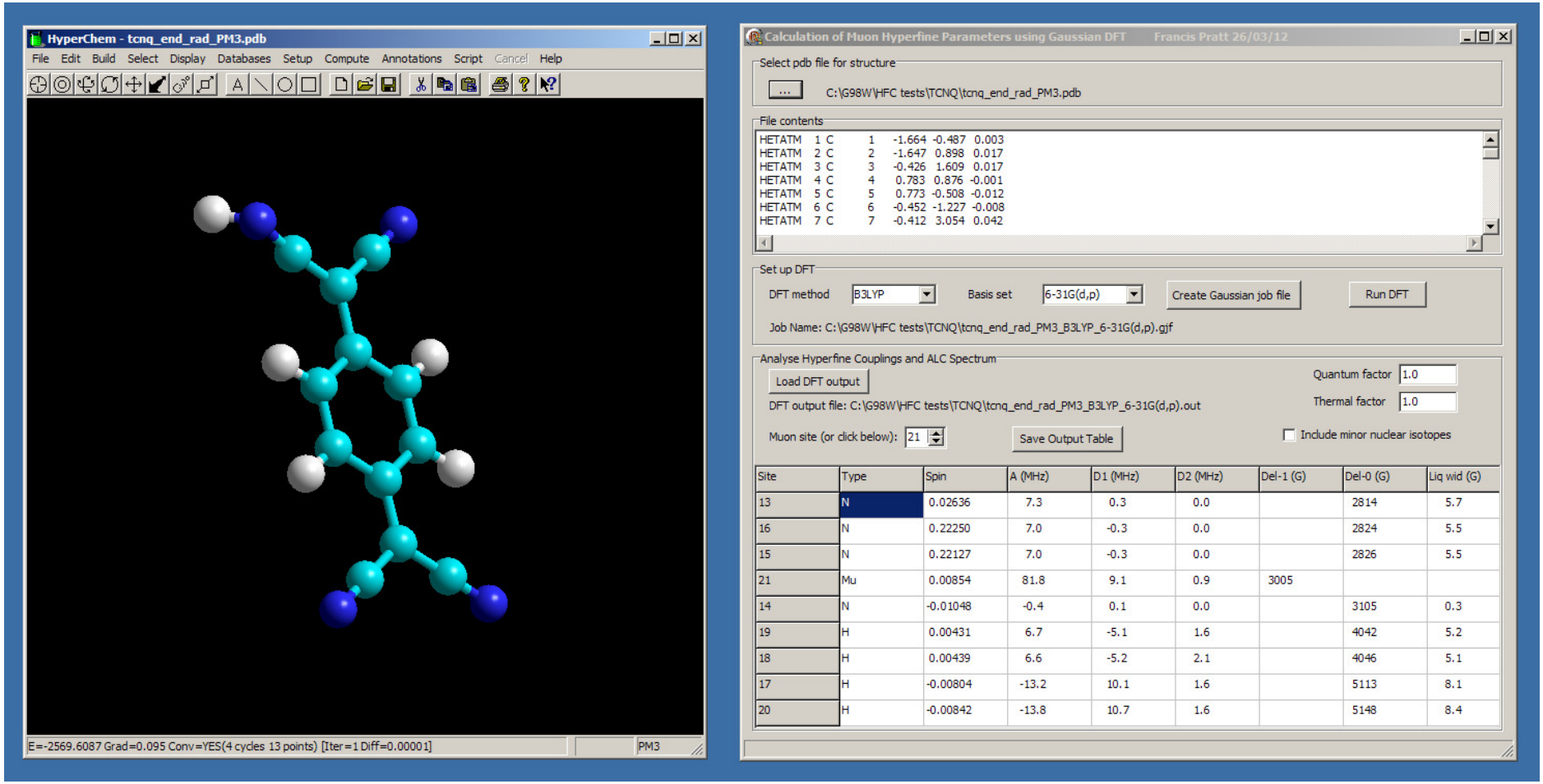




MusrGaussian

- Tool for ALC spectroscopy of molecular muon radicals
- Pragmatically optimised hybrid method:
  1. Semi-empirical UHF/PM3 for relaxed radical structure
  2. Single point DFT (UB3LYP) for spin density
  3. Calculate fully anisotropic HFC tensor from DFT spin density
  4. Simulate ALC spectral lines using WiMDA/Quantum

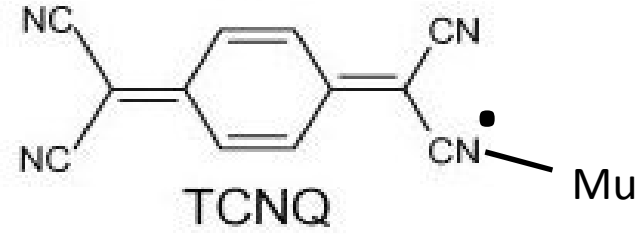
MusrGaussian

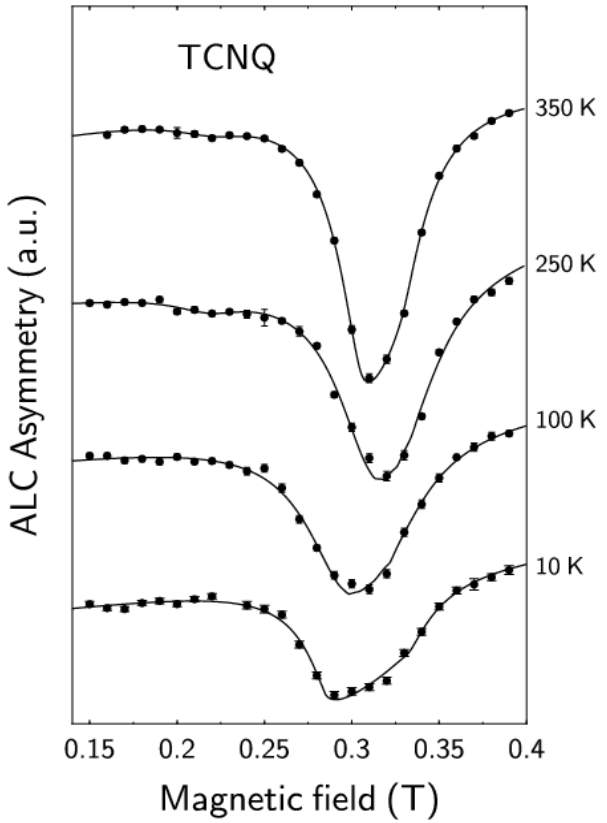


Optimal Calculation Level

	A	D_1	D_2	cost
Experiment (10 K)	**82**	**10.2**	**0**	
STO-3G	77	10.4	0.9	14
3-21G	72	10.9	0.9	30
6-31G	88	10.0	0.9	40
6-31G(d,p)	82	9.1	0.9	120
SVP	73	9.4	0.9	149
cc-pVDZ	**75**	**9.0**	**0.9**	**177**
(ZP corrected)	**82.5**	**10.4**		
cc-pVTZ	83	8.8	0.9	2332

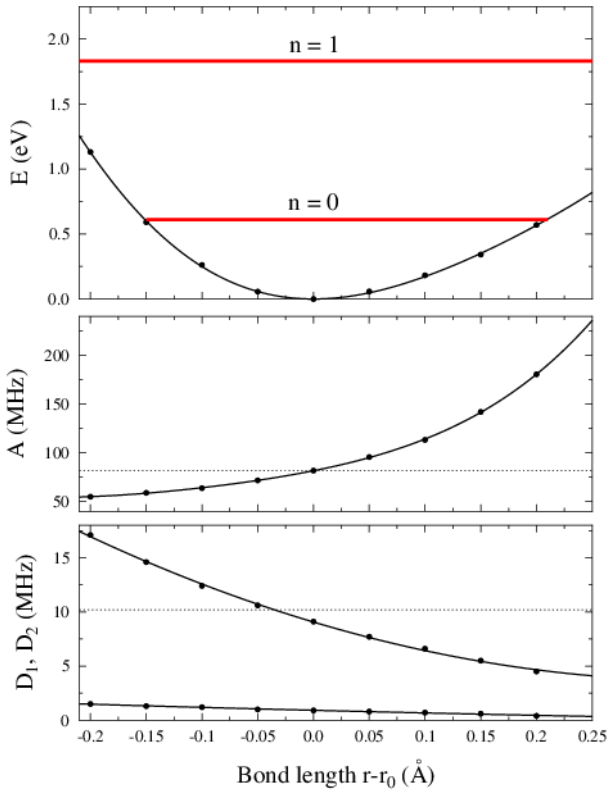
Table 1 *Comparison of measured hyperfine parameters in MHz for TCNQ with DFT estimates made using the B3LYP functional with progressively more costly basis sets. When the numerically calculated zero point quantum corrections of 1.10 for A and 1.15 for D_1 are applied, cc-pVDZ provides the best computational accuracy.*





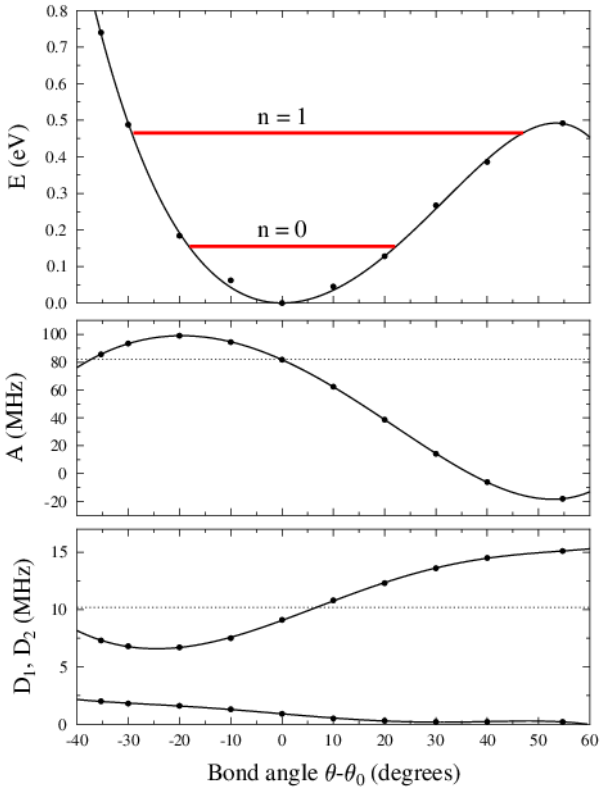
Quantum Zero Point Corrections

Bond Stretch



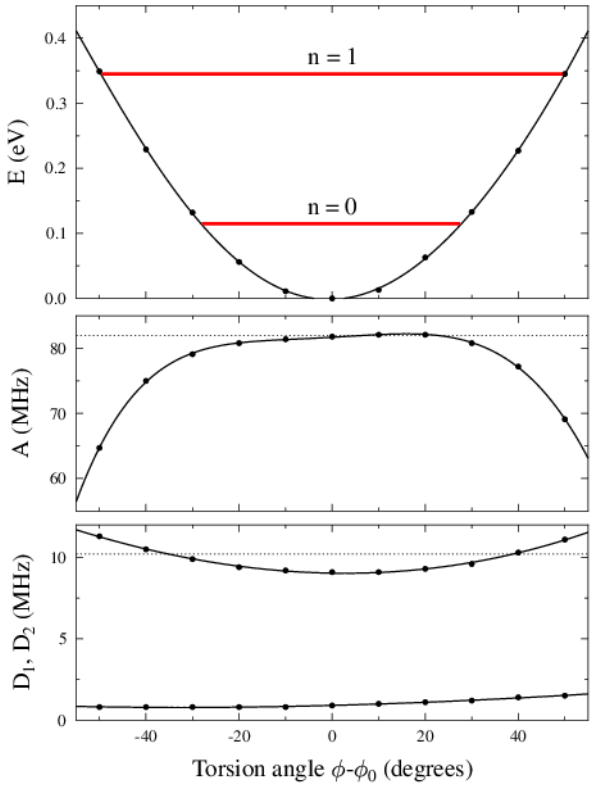
$QF_A = 1.21$

Bond Bend



$QF_A = 0.92$

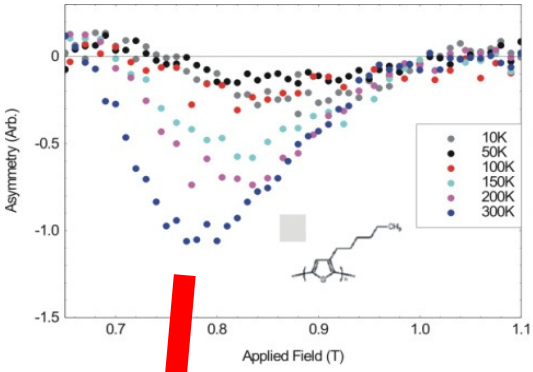
Bond Torsion



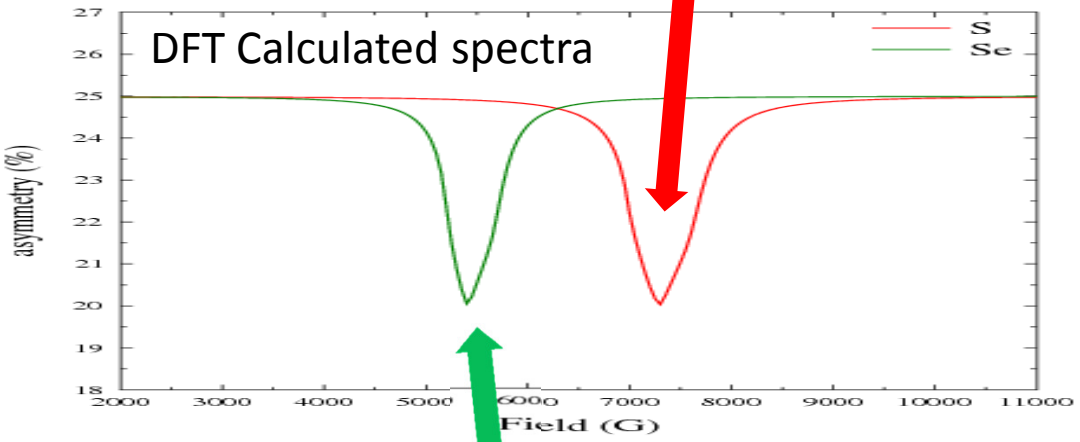
$QF_A = 0.99$

Overall $QF_A = 1.10$

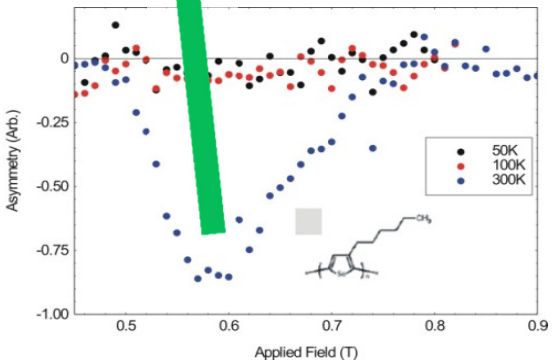
Some Polymer Examples



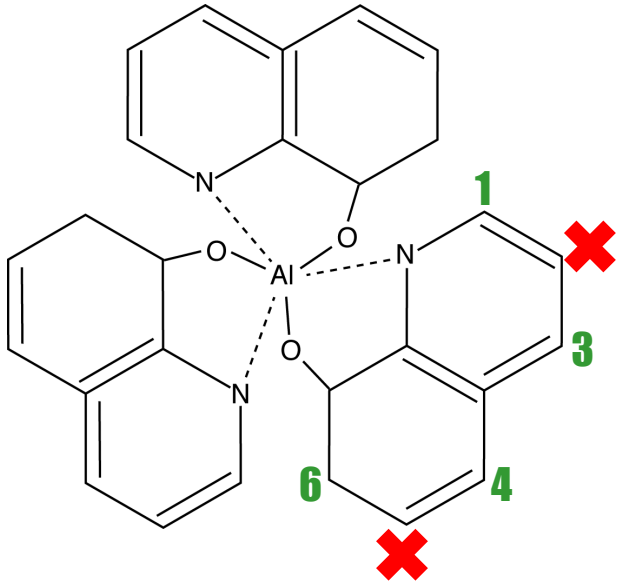
Polythiophene

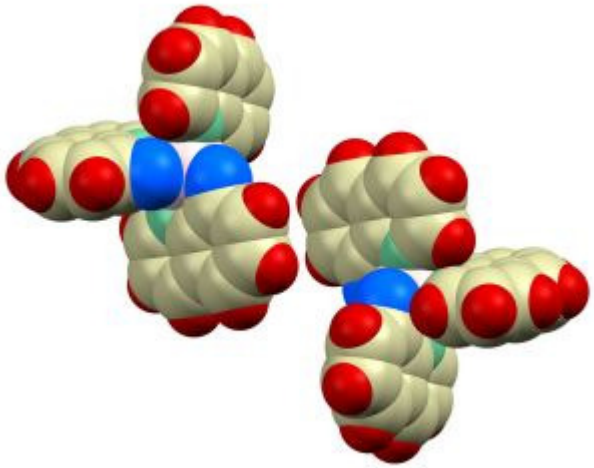


Polyselenophene



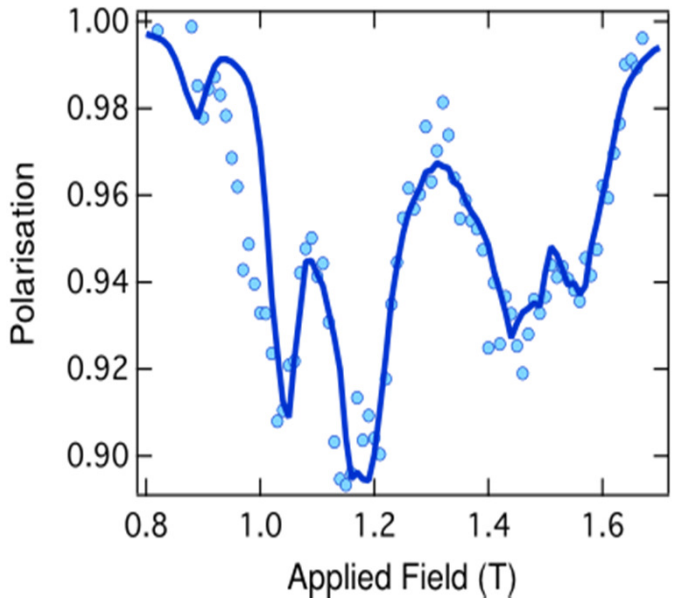
Example of a Larger Molecule : Alq_3





Full HFC tensor for 36 radicals

	Pratt							Data
	A1	A2	B1	B2	C1	C2	Ave_P	Ave_{dat}
Site 1	427.2	416.2	449.3	411.1	420.7	393.7	419.7	420.0
Site 2	498.9	484.9	501.4	491.6	467.2	513.8	493.0	-
Site 3	380.1	381.5	405.2	357.5	374.8	323.4	370.4	386.0
Site 4	284.9	297.4	291.4	311.8	281.3	241.3	284.7	292.5
Site 5	573.2	580.5	546.7	560.3	506.0	595.0	560.3	-
Site 6	330.4	337.1	372.4	344.7	327.9	312.3	337.5	329.0



Future Development

- Integrate ALC spectrum generation and viewing
- Links to enable use as a fit function in WIMDA/MANTID
- Move over to non-commercial code for generating the semi-empirical structure and DFT spin density
- Further work on the zero point spatial averaging effects
- Extend to thermal averaging effects in finite T